Optical and Surface Structural Properties of Mn^{2+} Doped ZnSe Nanoparticles

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Abstract

Semiconductor nanoparticles have been studied extensively because of their potential application in electronic devices and the opportunity they offer to study the effects of quantum confinement. A unique subset of semiconductor nanoparticles is doped semiconductor nanoparticles. Hines et al.[1] were the first to report the synthesis of highly luminescent mono-disperse undoped ZnSe nanoparticles. Shortly afterward Suyver et al.[2] and Norris et al.[3] synthesized Mn2+ doped ZnSe nanoparticles. Their results suggest that the Mn2+ ion incorporates primarily into the center of the nanoparticle and that the luminescence of the material is dependent upon the Mn2+ concentration in the particle. The presence of Mn2+ defect sites and their effect on the luminescence was not fully addressed.
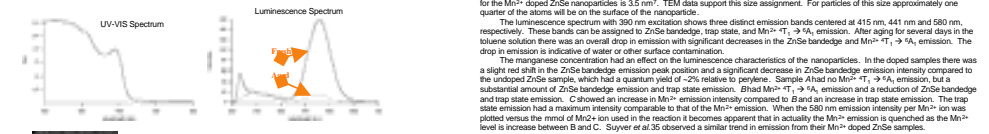
In our experiment[4] four ZnSe nanoparticles samples, one with low Mn2+ concentration (A), one with an intermediate Mn2+ concentration (B), one with a high Mn2+ concentration (C), and one with no Mn2+, were synthesized. The sample with no Mn2+ had a sharp ZnSe bandedge emission peak and a quantum yield of ~2%. The samples with Mn2+ had a significant decrease in bandedge emission. Sample A had no Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission, but showed some ZnSe bandedge emission and trap state emission. Sample B had Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission and a further reduction in ZnSe bandedge emission and trap state emission. Sample C showed an increase in the Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission, a dramatic increase in trap state emission, and essentially no ZnSe bandedge emission. In order to better understand these observations XAFS data were taken. The XAFS indicated that there was a reduction in the Zn and Mn first neighbor Se coordination from the bulk value but a lack of a reduction in the Se first neighbor coordination. This suggests that the core of the nanoparticles resembles that of bulk ZnSe, and the surface of the particle has a higher concentration of metal atoms. We propose that the surface Mn2+ possessed an octahedral geometry, and the overall low emission quantum yield is primarily due to the presence of Mn2+ on the particle surface.

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Synthesis of ZnSe:Mn Nanoparticles

X mmol Mn Acetate

HDA ~280° 2-6 hrs

All chemicals were acquired from Alfa-Aesar or Aldrich and were used without further purification. The synthetic method used was a modification of that developed by Cumberland[5] (Me4N)4[Zn10Se4(SPh)16]:Mn2+, molecular clusters were prepared following the procedure of Dance[6]. 6.3462 g of (Me4N)4[Zn4(SPh)10]. 0.6734 g of Se powder and varying amounts of manganese acetate were dissolved in 50 mL of N,N-dimethylformamide (DMF). Three different (Me4N)4[Zn10Se4(SPh)16]:Mn2+ molecular clusters were prepared, each with a different amount of manganese acetate. Sample A, B, and C had 0.0228 g (~0.6%), 0.2857 g (~6%) and 2.1675 g (~37%) of manganese acetate, respectively. The solution was allowed to sit for several minutes. Then it was filtered to remove any unreacted Se. Approximately 0.6 g of the (Me4N)4[Zn10Se4(SPh)16]:Mn2+, cluster were added to 80 mL of hot HDA, which had been previously kept under vacuum at 120 oC for two hours. Once the clusters had dissolved, the temperature was raised slowly to 280 oC. Particle growth was monitored by UV-VIS and luminescence spectroscopy, and the temperature was modulated between 200 oC and 280 oC to control the rate of particle growth. When the desired particle size was achieved, as determined by UV-VIS spectroscopy, the particles were annealed at 180 oC overnight.

To extract the particles from solution, the reaction solution was cooled to 80 oC and then poured into 100 mL of methanol, immediately forming a white precipitate. The mixture was centrifuged, and the methanol was discarded. The remaining white powder was dissolved in toluene. Additionally, the nanoparticle solution was filtered, and the toluene was evaporated. The nanoparticle powder was then washed with warm dry methanol, dissolved in heptane, and filtered. All of the nanoparticles were grown to the same size as determined by UV-VIS. Undoped ZnSe nanoparticles were also prepared by following the method of Cumberland[5].

References

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Optical Properties of ZnSe:Mn Nanoparticles

UV-VIS Spectrum

Luminescence Spectrum

The sharp exciton absorption peak centered at 395 nm in the UV-VIS spectrum of the final product in toluene is an indication that mono-disperse particles were produced. The position of the absorption maximum for the exciton peak suggests that the average particle diameter for the Mn2+ doped ZnSe nanoparticles is 3.5 nm7. TEM data support this size assignment. For particles of this size approximately one quarter of the atoms will be on the surface of the nanoparticle.

The luminescence spectrum with 390 nm excitation shows three distinct emission bands centered at 415 nm, 441 nm and 580 nm, respectively. These bands can be assigned to ZnSe bandedge, trap state, and Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission. After aging for several days in the toluene solution there was an overall drop in emission with significant decreases in the ZnSe bandedge and Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission. The drop in emission is indicative of water or other surface contamination.

The manganese concentration had an effect on the luminescence characteristics of the nanoparticles. In the doped samples there was a slight red shift in the ZnSe bandedge emission peak position and a significant decrease in ZnSe bandedge emission intensity compared to the undoped ZnSe sample, which had a quantum yield of ~2% relative to perylene. Sample A had no Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission, but a substantial amount of ZnSe bandedge emission and trap state emission. B had Mn2+ $^4T_1 \rightarrow {}^6A_1$ emission and a reduction of ZnSe bandedge and trap state emission. C showed an increase in Mn2+ emission intensity compared to B and an increase in trap state emission. The trap state emission had a maximum intensity comparable to that of the Mn2+ emission. When the 580 nm emission intensity per Mn2+ ion was plotted versus the mmol of Mn2+ ion used in the reaction it becomes apparent that in actuality the Mn2+ emission is quenched as the Mn2+ level is increase between B and C. Suyver et al.35 observed a similar trend in emission from their Mn2+ doped ZnSe samples.

References

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- Direct Band Gap Semiconductor
- Band Gap (Bulk)= 2.58 eV (~481nm)
- Exciton Radius = 7.1 nm

TEM Micrograph of synthesized particles

Mn2+ profoundly effects Emission of ZnSe Nanoparticles

Mn2+ Emission quencher

The EXAFS of ZnSe:Mn

ZnSe:Mn (~0.6% Mn2+)   ZnSe:Mn (~6% Mn2+)   ZnSe:Mn (~37% Mn2+)

A comparison of the fitted XAFS parameters for samples A, B, and C do not reveal any strong trends that could be the effect of an increased Mn2+ concentration; however, there are some subtle differences in the Mn K-edge data. The Zn-Se distance is the same as bulk, as are the Zn-Zn and Se-Se distances. However, the Mn-Se distance is shorter than that of bulk Mn2+ doped ZnSe as is the Mn-Zn distance. The necessity to fit the second shell data with two N-N shells suggests that there are two types of second neighbors in nanoparticles, with one type (') being more disordered than the other. In the Zn and Se K-edge data the amount of disorder in these shells does not change with increasing Mn2+ concentration, but in the Mn K-edge data sample C, the high Mn2+ concentration sample, has the lowest level of disorder for these shells. The necessity to fit the Zn and Mn K-edge data with a Metal-O shell, and the lack of such a shell in the Se K-edge data suggest that the surface of the particle is composed primarily of Zn and Mn atoms. Further more the decline in Mn-Se coordination number with increasing Mn2+ and the Mn-Se coordination being smaller than the Mn-O coordination suggests that most of the Mn2+ ions lie close to the surface of the nanoparticle. The large Mn-O coordination number also suggests that there could be Mn2+ atoms on the surface with octahedral geometry.

The Mn K-edge XAFS suggests that a significant number of the Mn2+ ions in the nanoparticles occupy the Zn2+ site in the lattice, since the first and second neighbor coordination shell can be fit to a model of Mn2+ in the Zn2+ lattice site. However, the Mn2+ ions lack a full first shell coordination of Se, which is an indication of the presence of Mn2+ on the surface of the nanoparticles. The Mn-Se shell coordination number is smaller than the Zn-Se shell coordination number, indicating a significant portion of the Mn2+ ions occupy a region close to the particles surface. An Mn-O first coordination shell was added to better fit the data; however, since O and N are similar in atomic number, this shell could be a metal-N shell resulting from the coordination of HDA to the nanoparticle surface. The sum of the Mn-Se and Mn-O coordination number gives a slightly larger first neighbor coordination number than expected for Mn2+ in a tetrahedral environment. This would suggest that the surface Mn2+ has a different geometry than that of the interior. Since physically only one HDA molecule bonds to one surface metal atom of the nanoparticle, the additional atoms modeled most likely belong to an oxygen species such as OH- or O2-. Mn2+ in MnO has octahedral geometry and the Mn-O bond distance determined from the fitting is consistent with that of Mn-O. Thus the surface Mn most likely posses octahedral geometry, due to the additional O coordination, while the interior Mn is of tetrahedral geometry.

1st Model for ZnSe:Mn Nanoparticles

Bulk-like ZnSe Core

Metal Ion Surface

~_ of all atoms on surface

$$S_n = 1/12 \, (10n^3 + 15n^2 + 26n + 12) \text{ for even values of n}$$
$$S_n = 1/12 \, (10n^3 + 15n^2 + 26n + 9) \text{ for odd values of n}$$

n = number of shells
S_n= number of atoms in shell n

2nd Model for ZnSe:Mn Nanoparticle

Bulk-like ZnSe Core

Amorphous Surface Composed of Metal Ions

Surface contaminants

Interior Mn2+ T_d

Surface Mn2+ O_h

The ESR Spectra of ZnSe:Mn

ESR Spectrum of ZnSe:Mn ~6% Mn2+

ESR Spectrum of ZnSe:Mn ~37% Mn2+

The local environment of the Mn2+ ion in the nanoparticles and precursor clusters was probed using XAFS and ESR. The ESR signal of the Mn2+ doped ZnSe nanoparticle B showed the classic six-line hyperfine splitting pattern of Mn2+. The hyperfine coupling constant was 61.87 x 10-4 cm-1, which is consistent with reported values for Mn2+ doped ZnSe in nanoparticles and bulk material36. However, superimposed upon this pattern is another six-line splitting pattern with a hyperfine coupling constant of 63.30 x 10-4 cm-1, which, in Mn2+ doped ZnS, has been attributed to Mn2+ at interstitial or surface sites of octahedral geometry in the nanoparticle lattice5. The slight broadening of the ESR spectrum suggests that exchange coupling maybe occurring in this sample. The broadening was more pronounced in sample B, which suggests stronger exchange interactions are occurring. Sample A had no ESR signal. The ESR signal from the nanoparticles has three distinct features: i) a six-line hyperfine splitting pattern due to Mn2+ substituting for a Zn2+ ion in the lattice, ii) exchange interaction, and iii) a six-line splitting pattern due to Mn2+ occupation of a site other than the Zn2+ lattice site. This splitting pattern has been observed in other Mn2+ doped II-VI nanoparticles9.11, and this second Mn2+ site has been attributed to Mn surface or interstitial site of octahedral symmetry.

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Conclusion